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STRESS CORROSION CRACKING OF URANIUM ALLOYS

Walter F. Czyrklis, et al

Army Materials and Mechanics Research Center
Watertown, Massachusetts

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ABSTRACT

The stress corrosion cracking behavior of U-3/4% Ti, and AMMRC uranium alloys 3 4% Quad, 1% Quad, and 1% Quint have been studied utilizing a linear elastic fracture mechanics approach. The threshold stress intensities for stress corrosion crack propagation for these alloys have been determined in distilled H_2O and NaCl solutions containing 50 ppm Cl^- and 21,000 ppm Cl^-. All of the alloys studied may be classified as very susceptible to SCC in aqueous solutions since they exhibit SCC in distilled H_2O (<1 ppm Cl^-) and have low K_{ISCC} values in NaCl solutions. Crack extension in all of the alloys in all environments was transgranular and failure occurred by brittle quasi-cleavage fracture in NaCl solution. (Authors)

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INTRODUCTION

The superior armor-piercing capabilities and ballistic properties of high density depleted uranium alloys make them prime candidates for artillery applications involving penetrators and nuclear ammunition. Many of these alloys, however, are susceptible to stress corrosion cracking (SCC) in a variety of environments.[1-7]

Stress corrosion cracking service failures, in general, result from the superposition of residual stresses in the system and the applied design stresses, or frequently from residual stresses alone. Table 1 lists some of the fabrication processes which leave high residual stresses in an alloy component. Several of these processes may be applicable to both penetrator and nuclear shell applications. One example is the XM-673 projectile, where an important consideration is the resistance of the uranium alloy shell material to environmentally induced crack growth in the region of pins (steel) which are retained by interference fit. A state of residual tangential tension exists around the pins which in combination with the effects of an aggressive environment can cause crack propagation during the period of time between manufacture and firing. Utilizing a linear elastic fracture mechanics approach, the uranium alloy shell material threshold of resistance to SCC (K_{Iscc}) can be determined.

This study was carried out to determine the critical threshold intensity for SCC, K_{Iscc}, of several uranium alloys which are candidates for penetrator and nuclear shell applications. The data reported here are for alloys in the as-extruded condition only and will serve as base-line data for future studies involving the solution-treated-and-aged alloys.

EXPERIMENTAL PROCEDURE

Materials

The uranium alloys studied include the 3/4% Ti, 3/4% Quad, 1% Quad, and the 1% Quint compositions. These alloys were in the as-extruded condition and their chemical analyses and mechanical properties are listed in Table 2 and 3. It should be noted that the 1% Quint alloy had the highest strength while the 3/4% Quad alloy had the highest elongation and reduction of area (ductility). The 3/4% Ti alloy had the lowest strength and had relatively low ductility.

Microstructures of the alloys are shown in Figure 1. The 3/4% Ti alloy contains some martensite which is due to the high M_s temperature, even though it is air cooled from a high extrusion temperature. Although the alloy is primarily alpha uranium, some beta uranium (identified by X-ray diffraction) is present because of slow cooling through the two-phase region. The black specks are probably U_2Ti intermetallic. The structure for the 3/4% Quad alloy is primarily alpha and

1. PETERSON, C. A. W. *A Stress Cracking Study of a Gamma Extruded U-8 wt % Mo-0.05 wt % Ti Alloy.* UCRL-14132, April 1965.
2. WHITLOW, G. A. *Stress Corrosion of Uranium Alloys.* AWRE-O-49/66, July 1966.
3. MAGNANI, N.J., and ROMERO, H. *Environmental Cracking of Mulberry.* Sandia Corporation, SC-TM-69-253, April 1969.
4. MAGNANI, N. J. *Stress Corrosion Cracking of Uranium Alloys.* Presented at NACE Spring 1970 Meeting.
5. MAGNANI, N. J. *Stress Corrosion of Mulberry.* Corrosion, v. 26, 1970, p. 406.
6. GREENSPAN, J., and FITZPATRICK, R. *Delayed Cracking and Corrosion Resistance of Some Uranium Alloys.* Army Materials and Mechanics Research Center Interim Report PDD-1, 24 September 1969.
7. MAGNANI, N. J. *The Effects of the Environment on the Cracking Behavior of Selected Uranium Alloys.* Presented at the NACE 1972 Meeting.

Table 1. FABRICATION PROCESSES WHICH LEAVE HIGH RESIDUAL STRESSES

Welding
Spinning
Punching
Deep Drawing
Riveting
Overtorquing Threaded Joints (Particularly Tapered Threads)*
Overtorquing Nut, Bolt and Capscrew Connections*
Inserting Oversize and Dissimilar Metal Bushings into Fittings*
Pull-Up in the Case of Mismatched Rivets or Holes
Caulking of Riveted Joints to Prevent Leaks
Improper Heat Treatments*

*Most applicable to our applications

Table 2. CHEMICAL ANALYSIS OF URANIUM ALLOYS

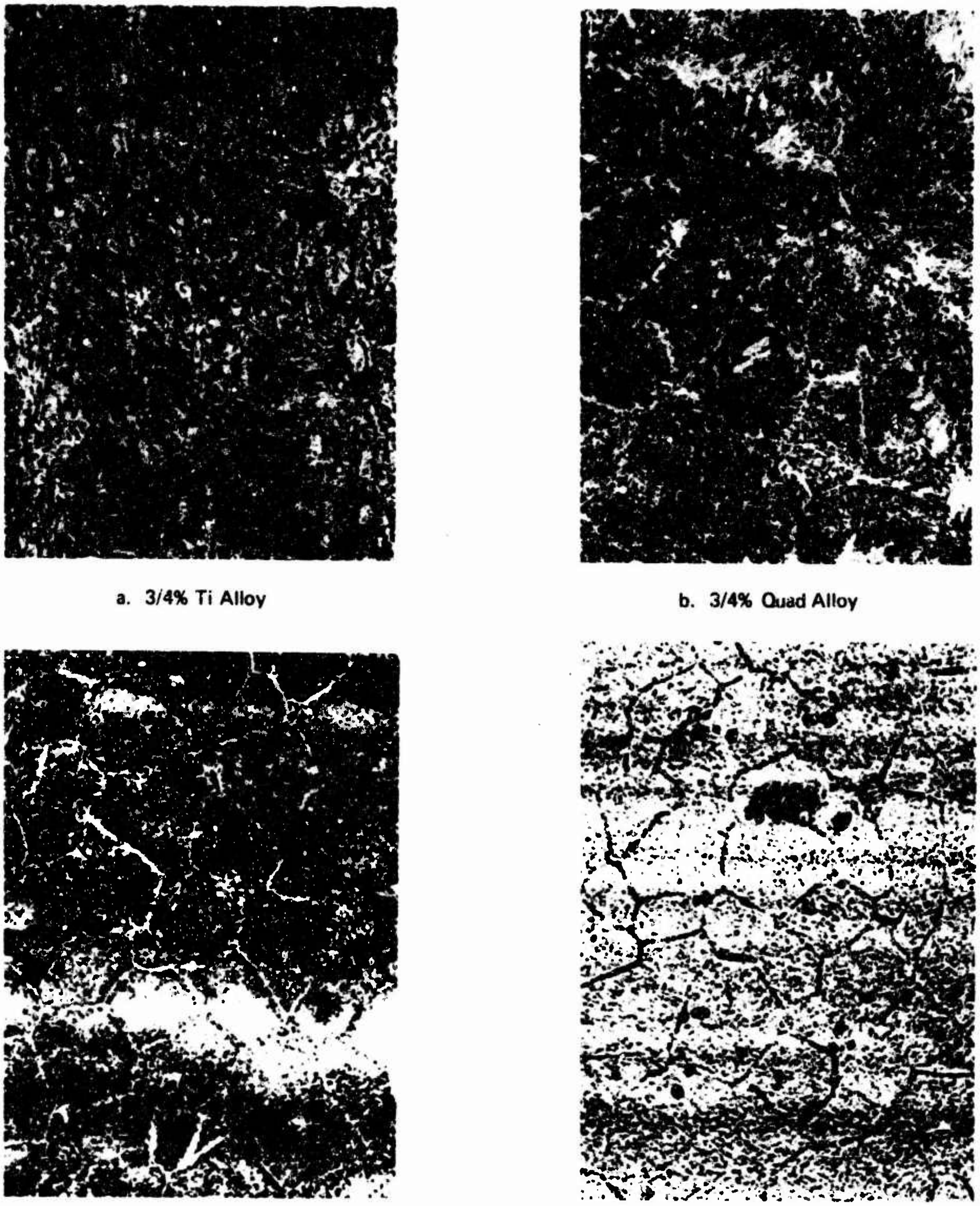
	ppm by wt				wt %				
Alloy	C	H	O	N	Mo	Nb	Zr	Ti	V
3/4% Ti	<10	2.4	20	7	-	-	-	0.70	-
3/4% Quad	50	1.6	40	54	0.73	0.74	0.70	0.49	-
1% Quad	22	4.4	74	-	1.03	1.04	0.98	0.62	-
1% Quint	59	-	-	23	1.00	1.00	0.94	0.47	0.57

Table 3. MECHANICAL PROPERTIES OF URANIUM ALLOYS

Alloy	UTS ksi	0.2% YS ksi	Elon. %	R.A. %	Hardness R_C
3/4% Ti	161.6	88	4.5	4.6	32
3/4% Quad	200	111.5	16.5	25.4	41
1% Quad	234	170	8.0	20.5	47
1% Quint	281.4	236	3.5	4.6	52

shows large recrystallized grains which probably were prior gamma grains. A second, light etching phase is present at the grain boundaries. Another phase appears to be finely distributed throughout the grains and inclusions of varying shape are also present. The microstructure of the 1% Quad alloy is similar to that of the 3/4% Quad alloy but shows evidence of banding. The 1% Quint alloy structure is primarily alpha uranium and shows large recrystallized equiaxed grains. A second, dark etching phase appears to outline some of the grains in the direction of banding. Another phase or precipitate is distributed throughout the grains and both inclusions and larger scale inhomogeneities are evident.

The environments used were distilled H_2O (contained <1 ppm Cl^-) and 3.5% NaCl solution (>21,000 ppm Cl^-). A limited number of SCC tests were carried out in solutions containing 50 ppm Cl^- to determine the effect of Cl^- concentration. Reagent grade chemicals and distilled H_2O were used to prepare the solutions.



a. 3/4% Ti Alloy

b. 3/4% Quad Alloy

c. 1% Quad Alloy

d. 1% Quint Alloy

Figure 1. As-Extruded Uranium Alloys. Mag. 500X

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Specimens and Testing

The stress corrosion specimens (see Figure 2) which were single-edge notch specimens (6.0" × 0.35" × 0.35") were fabricated from 5/8"-diameter extrusions and are designated LR, that is, the specimens were cut with the long dimension parallel to the direction of maximum grain flow and notched so that crack growth and fracture will occur in the radial direction.

The test uses a precracked bar stressed as a cantilever beam. A sharp notch is machined across the rectangular bar specimen at mid-length, and is sharpened by fatiguing. The specimen is held in a rack horizontally (as shown in Figure 3) with the precracked central portion surrounded by a plastic bottle which contains the environment. One end of the specimen is clamped to the mast of the rack and the other end to an arm from which weights are suspended. To evaluate the alloy, the specimen is first stressed in air at increasing loads until it fractures. The data are reduced to stress intensity using the Kies equation shown in Figure 2. Having established the stress intensity for "dry" conditions, K_{Ic}, a specimen is similarly tested in distilled H_2O and NaCl solutions at a somewhat lower stress intensity. If the specimen did not fail within an hour, the stress intensity was increased by approximately 3% each succeeding hour until failure occurred and the time required for rupture was noted. Additional specimens were stressed at lower stress intensities for 12 to 24 hours to give a more valid value for K_{Iscc} which was determined from a plot of stress intensity versus time to failure. K_{Iscc} is the threshold stress intensity value for the onset of cracking.

Fractured surfaces were replicated by the plastic carbon technique and examined by electron microscopy. Chromium was used as a replica-shadowing material.

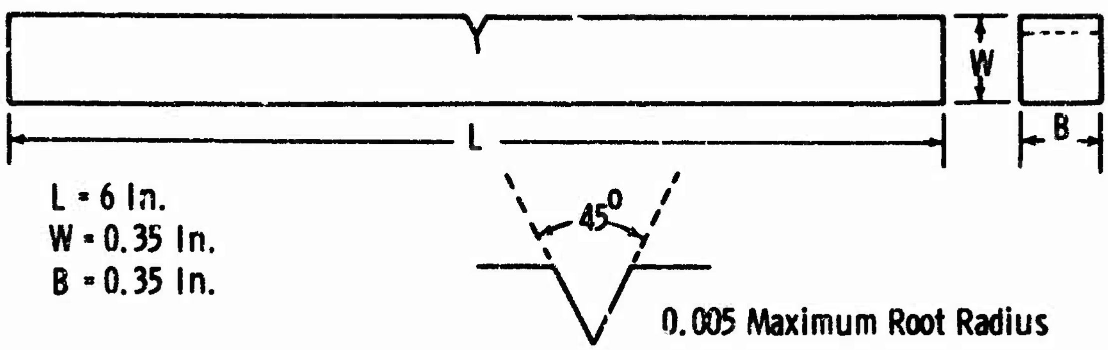
RESULTS AND DISCUSSION

K_{Iscc} Determination

Figure 4a contains plots of critical stress intensity versus time-to-failure for the alloys tested in distilled H_2O (<1 ppm Cl^-). The data show that K_{Iscc} is 40 ksi$\sqrt{in.}$ for the 3/4% Quad alloy, 28 ksi$\sqrt{in.}$ for the 1% Quad alloy, 21 ksi$\sqrt{in.}$ for the 3/4% Ti alloy, and 9 ksi$\sqrt{in.}$ for the 1% Quint alloy. The respective "dry air" values (see Table 4) are 47 ksi$\sqrt{in.}$, 32 ksi$\sqrt{in.}$, 24 ksi$\sqrt{in.}$, and 20 ksi$\sqrt{in.}$ For the testing times of 12 to 24 hours that were employed, the alloys showed relatively little susceptibility to SCC in distilled H_2O, except for the 1% Quint composition which exhibited greater susceptibility. Figure 4b shows similar plots for the alloys in a 3.5% NaCl environment (>21,000 ppm Cl^-). The K_{Iscc} values obtained, i.e., 15 ksi$\sqrt{in.}$ for the 3/4% Ti alloy, 12 ksi$\sqrt{in.}$ for the 3/4% Quad alloy, 7 ksi$\sqrt{in.}$ for the 1% Quad alloy, and 5 ksi$\sqrt{in.}$ for the 1% Quint alloy, indicate that all the alloys are very susceptible to SCC in this environment.

Additional tests were carried out with the 1% Quad and 1% Quint alloys in a NaCl solution containing only 50 ppm Cl^-. Threshold values similar to those found in the 3.5% NaCl environment (>21,000 ppm Cl^-) were obtained (see Figure 4c) indicating that the lower chloride concentration did not significantly affect (reduce) the susceptibility of these two alloys to SCC in NaCl. Figure 4 also shows that the susceptibility of the 1% Quint alloy to SCC in a NaCl solution containing 50 ppm Cl^- can be markedly reduced by adding 0.1M sodium nitrate to the solution. Electrochemical studies of unstressed specimens have shown that the uranium alloys studied cannot be anodically passivated in NaCl solutions containing 50 ppm Cl^- or greater and pitting of the alloys occurs.* However, the addition of 0.1M sodium

*M. LEVY and C. V. ZABIELSKI, AMMRC, unpublished data.



$$K = \frac{4.12\,(\alpha^{-3} - \alpha^{3})^{1/2} M}{B W^{3/2}} \quad \text{where} \quad \alpha = 1 - a/W,$$

a = crack length + notch depth

M = Moment
B = Thickness
W = Width

Figure 2. Specimen Geometry and Equation for K Values

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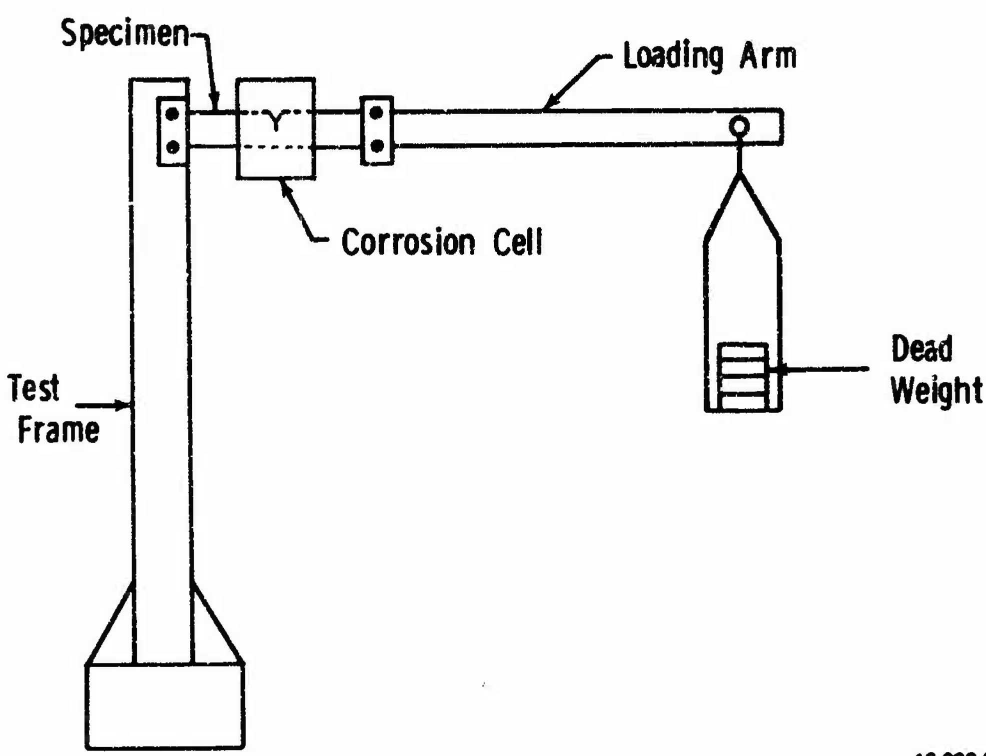

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Figure 3. Schematic Drawing of Cantilever Test Specimen and Fixtures

Table 4. SUMMARY OF URANIUM SCC RESULTS

	3/4% Ti 161.6 UTS 88 YS		3/4% Quad 200 UTS 111.5 YS		1% Quad 234 UTS 170 YS		1% Quint 281.4 UTS 236 YS	
Environment	K $ksi\sqrt{in.}$	Min. Thick. (in.)	K $ksi\sqrt{in.}$	Min. Thick. (in.)	K $ksi\sqrt{in.}$	Min. Thick. (in.)	K $ksi\sqrt{in.}$	Min. Thick. (in.)
Air	24	0.015	47	0.44	32	0.089	20	0.018
H_2O	21	0.011	40	0.32	28	0.068	9	0.004
3.5% NaCl	15	0.006	12	0.029	7	0.004	5	0.001
50 ppm Cl^-	-	-	-	-	9	0.007	5	0.001
50 ppm Cl^- +0.1M $NaNO_3$	-	-	-	-	-	-	16	0.011

Note: ASTM Minimum Thickness = $2.5 \left(\frac{K}{\sigma_y}\right)^2$

nitrate shifts the corrosion potential in the more noble direction, stifles the anodic reaction, and prevents pitting at potentials up to +0.6V versus SCE. The $NaNO_3$ also provides an inhibiting effect in the stress corrosion tests since the compound reduces the susceptibility of the alloy, that is, it increases the K_{Iscc} from 5 to 16 $ksi\sqrt{in.}$ which approaches the air value of 20 $ksi\sqrt{in.}$

A summary of all the results obtained are shown in Table 4 along with the ASTM recommended minimum thickness requirement. It should be noted that the specimen geometry for the alloys studied meets all the criteria for plane-strain conditions according to ASTM Specification E399-72 "Plane-Strain Fracture Toughness of Metallic Materials" except for the dry air value obtained for the 3/4% Quad alloy.

Fractography

Figure 5 presents high magnification replica fractographs for each alloy showing the effect of environment on the fracture mode. The predominant mode of failure for the 3/4% Ti alloy in air, distilled H_2O, and 3.5% NaCl solution is transgranular quasi-cleavage. The cleavage planes are broken up into small facets with coarse and ill-defined river markings and facets are joined by highly distorted regions. The fractograph for the 3/4% Quad alloy shows that the failure mode in air is transgranular plastic (normal) fracture. Note the round and equiaxed dimples. In distilled H_2O there is a dual-structured topography in the slow growth region. Areas of quasi-cleavage and ductile dimple fracture are observed. In the slow growth (SCC) region the predominant failure mode in 3.5% NaCl is quasi-cleavage.

The fracture mode for the 1% Quad alloy in air is mixed quasi-cleavage and dimple rupture. A similarly structured topography was observed in the slow growth region of the alloy in the distilled H_2O environment, while quasi-cleavage was the failure mode in 3.5% NaCl solution. Dimple rupture is the mode for the 1% Quint alloy in air, Figure 6. Note that the dimples are smaller than those observed in the 3/4% Quad alloy indicating that the Quint alloy is less ductile (see R.A. values in Table 3). In distilled H_2O the fracture consisted of a mixed quasi-cleavage and dimple rupture slow growth mode. The addition of

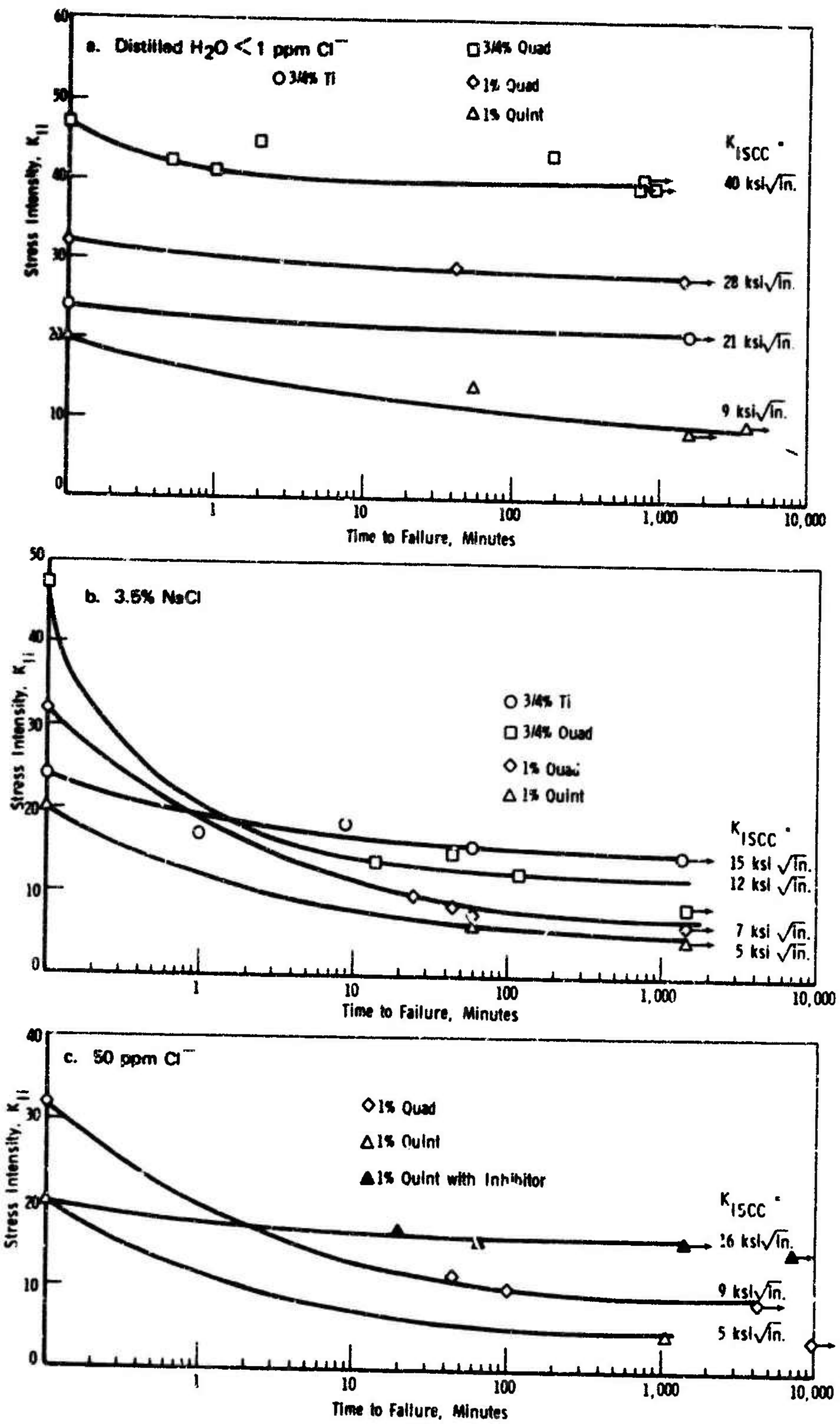

Figure 4. Stress Corrosion Cracking Behavior of Uranium Alloys in Various Environments

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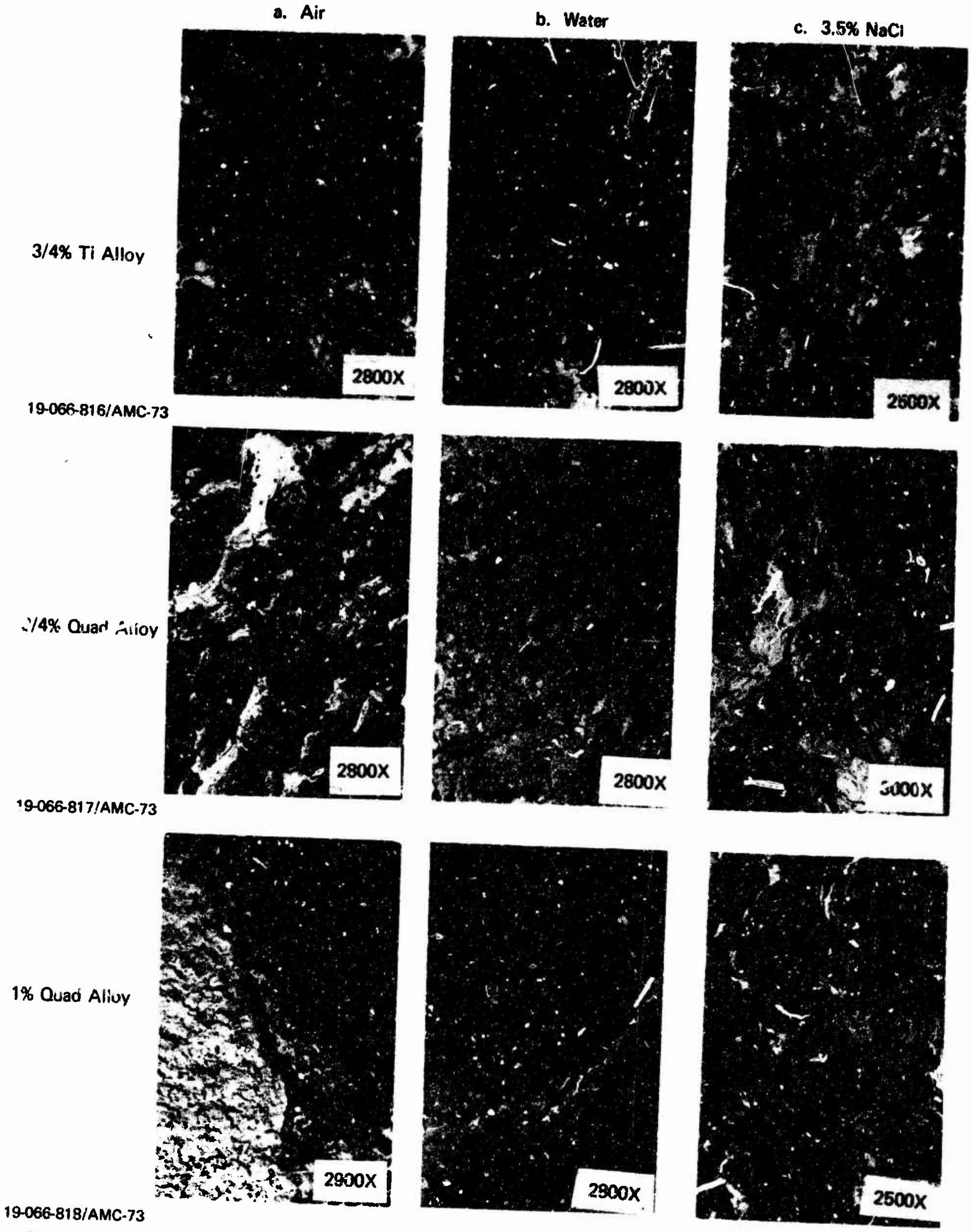

Figure 5. Electron Fractographs of Uranium Alloys Showing Fractures in (a) Air, (b) Water, and (c) 3.5% NaCl

a. Air - Mag. 2500X

b. H_2O - Mag. 3800X

c. 50 ppm Cl - Mag. 3000X

d. 50 ppm Cl + 0.1% $NaNo_3$ - Mag. 3500X

e. 3.5% NaCl - Mag. 3800X

Figure 6. Electron Fractographs of the 1% Quint Alloy Showing Fractures in Various Environments

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chloride ion (50 ppm and 21,000 ppm) to the distilled H_2O resulted in pure quasi-cleavage fracture while the addition of an inhibitor, $NaNO_3$, to the chloride solution (50 ppm Cl^-) produced the dual mode quasi-cleavage and dimple rupture topography observed in distilled H_2O. A summary of the influence of environment on the fracture behavior of the uranium alloys is contained in Table 5.

Magnani[7] reported the K_{Iscc} value was 25 to 30 ksi$\sqrt{in.}$ for U-0.5% Ti alloy tested in air and 22 ksi$\sqrt{in.}$ when tested in 50 ppm Cl^- solution. The alloy was in the metastable condition obtained by quenching from the gamma region. The stress corrosion fracture mode in both the air and the chloride environment was transgranular. Our data for the U-3/4% Ti alloy is quite similar although the Ti content is 0.20% greater. Magnani[7] observed that the relative susceptibility to intergranular cracking decreases as the alloy content decreases. It appears from his work that intergranular cracking is observed when the alloy content is 4-1/2% or greater while at lower alloy content the transgranular mode is operative. Our work supports this observation insofar as all the alloys tested had alloy contents less than 4.0% and the stress corrosion cracking failure mode was transgranular in all cases.

Table 5. SUMMARY OF THE INFLUENCE OF ENVIRONMENT ON THE FRACTURE BEHAVIOR OF URANIUM ALLOYS

	Environment				
	Air	H_2O	50 ppm Cl^-	21,000 ppm Cl^-	50 ppm Cl^- + $NaNO_3$
Alloy	Type of Fracture				
3/4% Ti	quasi-cleavage	quasi-cleavage		quasi-cleavage	
3/4% Quad	plastic fracture, normal mode (ductile dimple)	quasi-cleavage plus ductile dimple		quasi-cleavage	
1% Quad	cleavage facets plus dimples	cleavage facets plus dimples		quasi-cleavage	
1% Quint	normal plastic fracture smaller dimples than Quads	quasi-cleavage some dimples	quasi-cleavage	more cleavage-like	cleavage plus ductile dimple

Critical Flaw Depth

In Figure 7 the stress corrosion cracking threshold K_{Iscc} in air and aqueous environments is plotted as a function of yield strength to give an analysis of the relative merit of various alloy compositions.[8] The data in this figure can be related to critical flaw sizes for propagation of a stress corrosion crack by the Irwin equation, which gives the crack tip stress intensity for a surface flaw of arbitrary geometry:

$$K^2 = \frac{1.2\pi\sigma^2 a}{Q^2 - 0.212\left(\frac{\sigma}{\sigma_y}\right)^2} \tag{1}$$

where σ is the applied stress, a is the depth of the crack, Q is a shape factor for the crack, and σ_y is the yield stress. By assuming a ratio of applied stress to yield stress, the minimum critical flaw depth to propagate a stress corrosion crack can be expressed in terms of the material properties K_{Iscc} and σy. The straight lines representing flaw depths plotted in Figure 7 are based on the assumption of a long thin crack ($Q^2 = 1$), and $\sigma = \sigma_y$, for which equation (1) becomes:

$$a_{cr} = 0.2\left(\frac{K_{Iscc}}{\sigma_y}\right)^2 \tag{2}$$

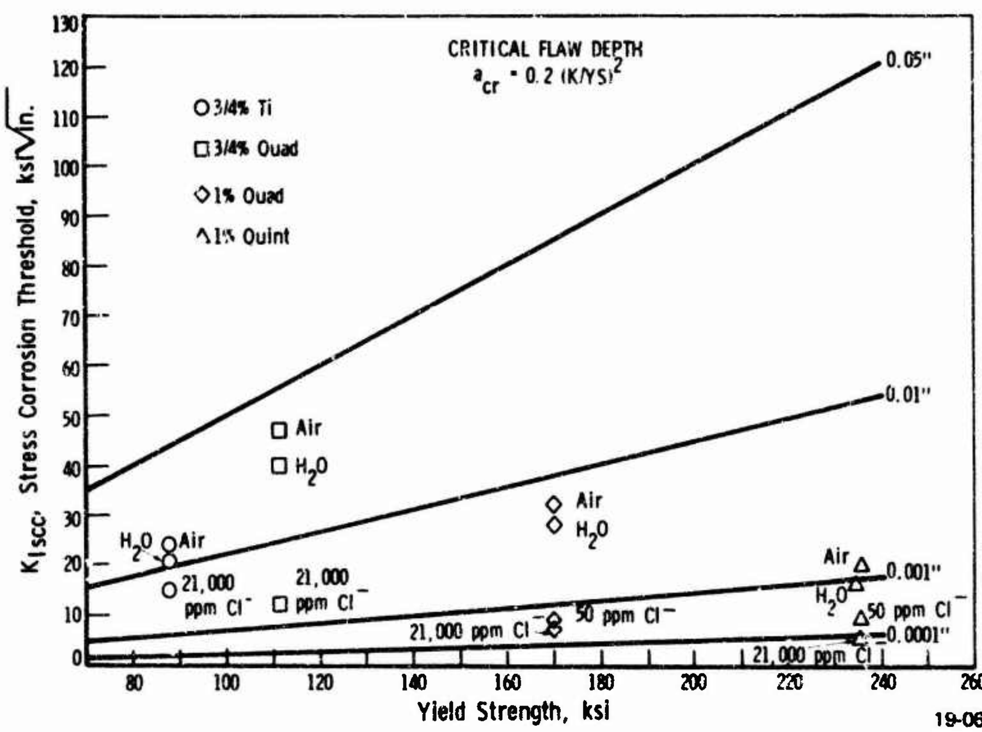

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Figure 7. K_{Iscc} for Uranium Alloys in Air, Distilled Water, and 3.5% Sodium Chloride, Shown as a Function of Yield Strength. Equation (2) is Plotted for Four Values of Crack Size.

8. BROWN, B. F., Editor. *Stress Corrosion Cracking in High Strength Steels and in Titanium and Aluminum Alloys.* Naval Research Laboratory, Washington, D. C., 1972, p. 10-12.

The assumption $\sigma/\sigma_y = 1$ represents the most conservative case. In applications where the applied stress derives solely from residual or fit-up stresses, σ/σ_y ratios on the order of 0.25 to 0.50 are probably more realistic. In that case the critical flaw depths shown in Figure 7 would be 20 times and 5 times larger than those computed from equation (2), respectively. The significance of this figure is that if one has a flaw size represented by one of the lines, an alloy whose K_{Iscc} falls above that line should be utilized if SCC is to be avoided.

For the "worst" case, $\sigma = \sigma_y$, the K_{Iscc} data which have been plotted in Figure 7 show that none of the alloys studied can tolerate a flaw as deep as 0.050" in any of the environments if the operative stress equals the yield strength. The critical flaw size for the 3/4% Ti alloy appears to be 0.010" in both air and H_2O. The alloy can tolerate a flaw as deep as 0.001" in 3.5% NaCl solution. The 3/4% Quad alloy can readily tolerate a flaw 0.010" deep in air and in H_2O. In 3.5% NaCl solution the tolerable crack depth is 0.001". Flaws as deep as 0.001" can be tolerated by the 1% Quad alloy in both air and H_2O, but in NaCl solutions the crack depth tolerance is reduced to 0.0001". The 1% Quint alloy, which is the most susceptible alloy, can tolerate a flaw as deep as 0.0001" in most environments. Based on crack depth tolerances the alloys can be listed in the following order of decreasing merit: 3/4% Quad alloy, 3/4% Ti alloy, 1% Quad alloy, and 1% Quint alloy. For a lower ratio of σ/σ_y, the magnitudes of the crack depth tolerances would increase, but the order of merit ranking would remain the same.

CONCLUSIONS

1. In relative terms all the alloys studied may be classified as very susceptible to SCC in aqueous solutions since they exhibit SCC in distilled H_2O and have low K_{Iscc} values in NaCl solution.

2. The alloys can be ranked in the following order of decreasing merit incorporating both the SCC resistance K_{Iscc} and the contribution which yield strength levels can make to SCC failure: 3/4% Quad alloy, 3/4% Ti alloy, 1% Quad alloy, and 1% Quint alloy.

3. SCC resistance usually decreases markedly with increasing strength level. In this respect the performance of the 3/4% Quad alloy is exceptional and the performance of the 1% Quint alloy is not surprising.

4. Sodium chloride provides an extremely aggressive environment for SCC of uranium alloys, even at a concentration of 50 ppm Cl^-.

5. The SCC resistance of the most susceptible alloy, the 1% Quint, can be significantly improved by adding sodium nitrate to the chloride solution.

6. Fractographic analysis of the stress-corroded specimens showed that crack extension in all of the alloys in all environments was transgranular. The 3/4% Ti alloy failed by brittle quasi-cleavage fracture in air, distilled H_2O, and NaCl

solution. The AMMRC Quad and Quint alloys exhibited fractographic ductile characteristics in air (dimple rupture). The distilled H_2O environment produced a mixed brittle and ductile topography while NaCl solution produced only brittle characteristics in these alloys.

FUTURE WORK

Similar studies will be carried out with these alloys in the solution-treated-and-aged condition. Applied anodic and cathodic potential as well as hydrogen permeation experiments will also be carried out in order to elucidate the SCC mechanism or mechanisms which may be operative.